

Photoluminescence of $\text{Gd}_2\text{O}_3\text{:Er}$ - based materials for conversion of solar energy

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Abstract. The spectral and luminescence properties of Er^{3+} activated Gd_2O_3 compacted powders have been investigated. There are several excitation channels of Er^{3+} luminescence: interband transitions, the energy transfer from Gd^{3+} ions and intracenter excitation. The quantum efficiency of the Er^{3+} ions luminescence under different excitation was calculated.

1. Introduction

Problems of modern energy, in particular, the growth of energy consumption and limited fossil resources, contribute to the development of alternative energy sources. Nowadays solar energy has broad prospects, therefore the majority of studies are focused on improving the efficiency of photovoltaic cells. It is known that the efficiency limit of most common photovoltaic cells based on single crystalline Si (c-Si) is estimated to be 32% (the Shockley–Queisser limit) due to mismatch between the solar spectrum and the Si absorption spectrum [1]. There are energy losses in Si solar cell such as thermalization (when photons with energy greater than Si band gap are absorbed and excess energy is lost as heat) and transmission (when photons with energy less than Si band gap are not absorbed). These losses can be reduced by using luminescent solar concentrators containing optically active centers [2]. The basic idea is better exploitation of the solar spectrum through the down-conversion (one high energy photon is converted into two or more lower-energy photons) and up-conversion (two or more low-energy photons combine to create one higher-energy photon) mechanisms. Luminescent solar concentrators represent the additional layers above (for down-conversion) or below (for up-conversion) solar cells (figure 1).

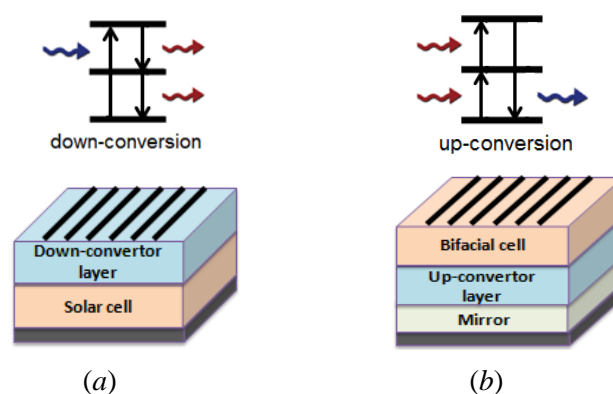


Figure 1. Basic principle and application of down-converter (a) and up-converter (b).



Rare-earth ions are of interest as optical centers in luminescent energy converter materials due to specialty of their energy levels structure in the visible, ultraviolet and infrared regions of the spectrum. Rare earth oxides are used as the host materials because of their optical and chemical properties (broad band gap, low phonon energy) and the ability of being easily doped with rare earth ions in high concentrations. It is known that solar energy conversion efficiency is determined by the quantum efficiency of optically active ions photoluminescence [3]. In present work the quantum efficiency of the Er^{3+} ions luminescence in host lattice Gd_2O_3 under different excitation was determined.

2. Samples and Methods

Compacted powder samples of $\text{Gd}_2\text{O}_3: \text{Er}^{3+}$ were prepared by sol-gel method at the Institute of Physics Polish Academy of Sciences, Warsaw, Poland. Crystal phase of Gd_2O_3 was identified as monoclinic with space group $C2/m$ (lattice parameters $a = 14.09 \text{ \AA}$; $b = 3.57 \text{ \AA}$; $c = 8.76 \text{ \AA}$) by powder XRD pattern. The photoluminescence and excitation spectra and luminescence decay kinetics were obtained at room temperature using a fluorescence spectrometer PerkinElmer LS 55. The temperature luminescence intensity dependence was investigated using a spectrometer McPherson.

3. Results and discussion

3.1 Emission and excitation spectra

Upon excitation at 220 nm (interband transition in host lattice Gd_2O_3) the emission spectrum of $\text{Gd}_2\text{O}_3: \text{Er}^{3+}$ demonstrates the typical Er^{3+} ions emission peaks at 522 and 544 nm originated from $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ to $^4\text{I}_{15/2}$ transitions respectively (figure 2) [4]. In addition, a lot of narrow lines with lower intensity are observed in the ultraviolet and visible regions of the emission spectrum. So the line photoluminescence spectrum is characteristic of TR^{3+} 4f-4f transitions that indicates uncontrolled TR^{3+} traces presence in $\text{Gd}_2\text{O}_3: \text{Er}^{3+}$ powder. In particular, emission bands at 487 nm (Pr^{3+}), 579 and 588 nm (Tb^{3+}), 612 and 621 nm (Eu^{3+}) were identified according to [5].

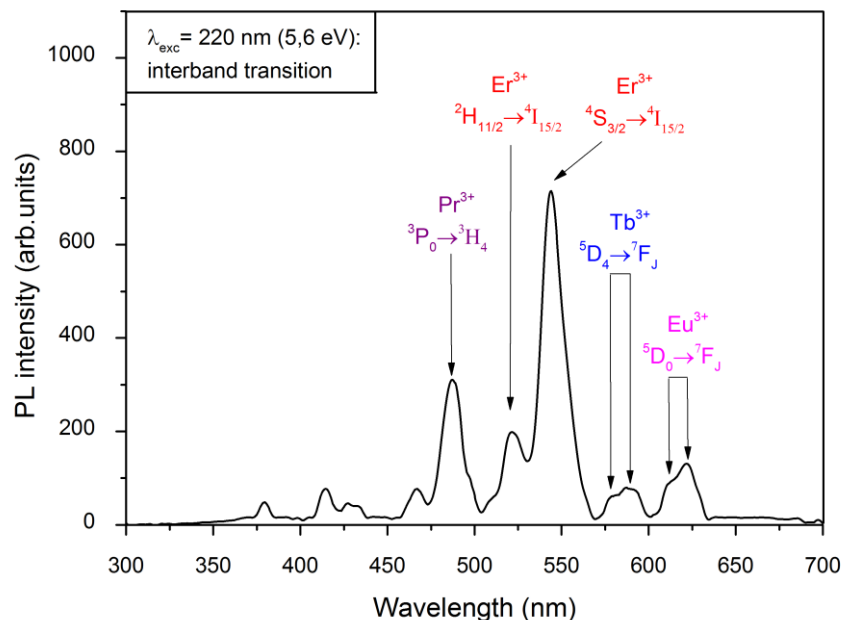


Figure 2. Emission spectrum of $\text{Gd}_2\text{O}_3: \text{Er}^{3+}$ upon excitation at 220 nm. The arrows indicate lines corresponding to Er^{3+} transitions and Pr^{3+} , Tb^{3+} , Eu^{3+} uncontrolled traces transitions. Unmarked lines interpretation is not available presently.

Excitation spectra monitored at 544 nm emission of Er^{3+} at different wavelength ranges are shown in figure 3. The lines at 409, 380 и 367 nm are assigned to the $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{9/2}$, $^4\text{G}_{11/2}$, $^2\text{G}_{9/2}$ intra-4f-4f transitions of Er^{3+} , respectively [6]. Excitation spectrum in the short-wave region demonstrated lines at 220, 247, 277 и 312 nm corresponded to the interband transition and intra-4f-4f transitions of Gd^{3+} from the ground state $^8\text{S}_{7/2}$ to the excited states $^6\text{D}_J$, $^6\text{I}_J$ and $^6\text{P}_J$ [4]. Excitation of Gd^{3+} ions through the mentioned above transitions in the region of Gd_2O_3 band gap indicate that such ions cannot be located at regular lattice positions and may be associated with intrinsic defects of host lattice Gd_2O_3 .

Intracenter excitation of Er^{3+} luminescence is dominant but the presence of Gd^{3+} transition lines in the excitation spectrum points out Gd^{3+} to Er^{3+} energy-transfer. So there are several excitation channels of Er^{3+} luminescence: interband transitions, the energy transfer from imperfect Gd^{3+} ions and intracenter excitation.

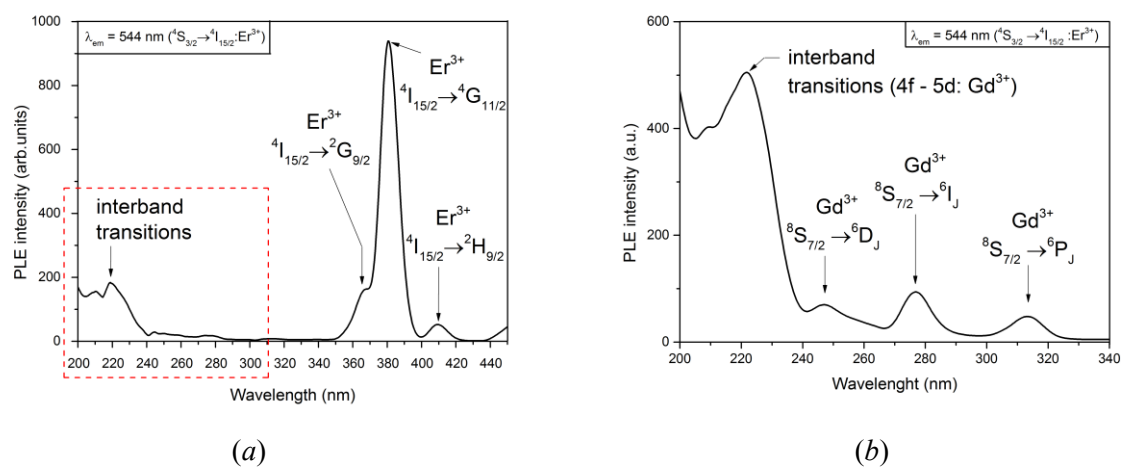


Figure 3. Excitation spectra at emission 544 nm ($^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$; Er^{3+}) in the wavelength range from 200 to 450 nm (a) and from 200 to 340 nm (b).

3.2 Emission decay curves and energy transfer

The emission decay curves of Er^{3+} $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition under different excitation are presented in figure 4. All the decay curves are described by double-exponential equation (1) [3]:

$$I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2), \quad (1)$$

where I is the luminescence intensity; A_1 and A_2 are constants; t is the time; τ_1 and τ_2 are decay time for exponential components.

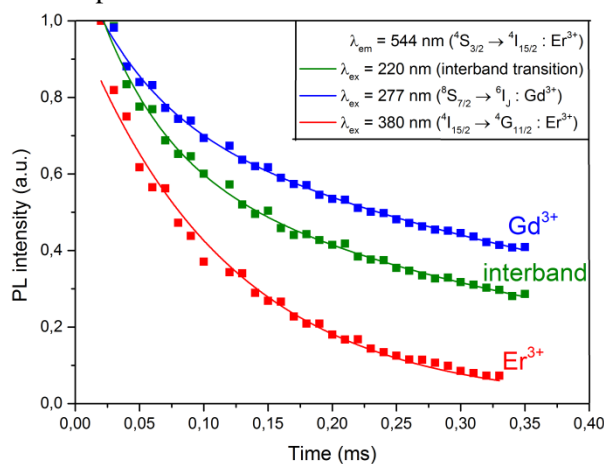


Figure 4. Luminescence decay of Er^{3+} $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition under intracenter excitation, interband excitation and excitation by imperfect Gd^{3+} ions. All curves are obtained at room temperature and approximated by double-exponential.

Because of non-exponential behavior of Er^{3+} luminescence decay, the average lifetime (τ) of Er^{3+} ion could be calculated using following equation (2):

$$\tau = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \quad (2)$$

The parameters of decay curves fitting and average decay times of Er^{3+} luminescence are listed in table 1.

Table 1. The parameters obtained from fitting data and calculated average lifetimes of Er^{3+} under different excitation.

| Excitation channel | A_1 | A_2 | τ_1 (ms) | τ_2 (ms) | τ (ms) |
|-------------------------------------|---------|---------|---------------|---------------|-------------|
| Intracenter excitation | 0.85559 | 0.73017 | 0.13111 | 0.01943 | 0.11857 |
| Interband transitions | 0.65838 | 0.57281 | 0.40587 | 0.05204 | 0.37036 |
| Excitation by Gd^{3+} ions | 0.38634 | 0.76739 | 0.05541 | 0.53693 | 0.51308 |

It is found that the decay time of Er^{3+} luminescence increases under interband excitation and excitation by Gd^{3+} ions. Possible mechanism of excitation energy transfer from Gd^{3+} to Er^{3+} are represented using energy level diagram (figure 5). The population of the Er^{3+} radiative level $^4\text{S}_{3/2}$ is carried out in several stages under indirect excitation. This fact confirm the increase decay time of Er^{3+} luminescence under this excitation type.

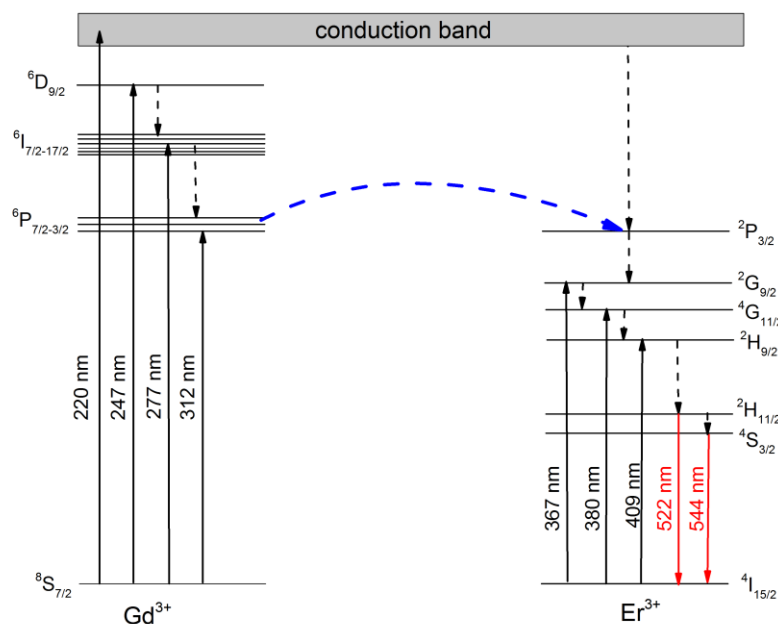


Figure 5. Schematic diagram of Gd^{3+} and Er^{3+} energy levels demonstrating the mechanism of energy transfer from the Gd_2O_3 host lattice and imperfect Gd^{3+} ions to the luminescent Er^{3+} centers.

3.3 Quantum efficiency calculation

Traditionally, the quantum efficiency is defined as ratio of the luminescence decay time to the its radiation component [7]. Using the interrelation between the decay time and its radiation and non-radiative components the analytical expressions for calculating the quantum efficiency of Er^{3+} ions luminescence under intracenter excitation (3) and excitation by Gd^{3+} ions (4) are obtained.

$$\eta_1 = \left(1 + \frac{C}{e^{E/kT}}\right)^{-1}, \quad (3)$$

where η_1 – quantum efficiency under intracenter excitation;

C – quenching constant;

E – activation energy.

$$\eta_2 = \gamma_{\text{Gd-Er}} \cdot \eta_1, \quad (4)$$

where η_2 – quantum efficiency under excitation by Gd^{3+} ions;

$\gamma_{\text{Gd-Er}}$ – efficiency of the energy transfer from Gd^{3+} to Er^{3+} .

The parameters of temperature quenching of the Er^{3+} luminescence are determined as a result of quenching curve fitting according to Mott's law ($E = 0.0685$ eV, $C = 14.907$). The Gd^{3+} to Er^{3+} energy transfer efficiency is estimated to be 80% as a typical value in the case of 1% acceptor rare-earth ions concentration [8]. On the basis of the obtained data the quantum efficiency of the Er^{3+} ions luminescence under intracenter excitation ($\eta_1=0,5$) and excitation by Gd^{3+} ions ($\eta_2=0,4$) are calculated.

4. Conclusion

The results indicate that the efficiencies of direct and indirect excitation of Er^{3+} ions luminescence are characterized by the same order. It is found that the most decay time of the Er^{3+} ions luminescence is observed under excitation by Gd^{3+} ions, however, the quantum efficiency in this case is less. It means that the major losses under indirect excitation take place at intermediate stages. So there is a reserve for minimizing these losses and the quantum efficiency of the Er^{3+} ions luminescence can be controlled by changes the defectiveness of host lattice Gd_2O_3 .

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